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**D-81679 München (DE)**(54) **Non-reducing dielectric ceramic composition.**

(57) To provide a non-reducing dielectric ceramic composition for multilayer ceramic capacitor, in which decrease of specific resistance and shortening of life time do not occur due to reduction of dielectric ceramic composition even when it is fired in neutral or reducing atmosphere and capacitance does not vary extensively due to temperature change, the non-reducing dielectric ceramic composition according to the present invention comprises 86.32 to 97.64 mols of BaTiO<sub>3</sub>, 0.01 to 10.00 mols of Y<sub>2</sub>O<sub>3</sub>, 0.01 to 10.00 mols of MgO, and 0.001 to 0.200 mol of V<sub>2</sub>O<sub>5</sub>. An additive containing 0.01 to 1.0 mol% of at least one or more of MnO, Cr<sub>2</sub>O<sub>3</sub>, or Co<sub>2</sub>O<sub>3</sub>, and further, an additive containing 0.5 to 10.0 mol% of {Ba<sub>A</sub>,Ca<sub>(1-A)</sub>}SiO<sub>3</sub> (where 0 ≤ A ≤ 1) may be added.

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## FIELD OF THE INVENTION

The present invention relates to a non-reducing dielectric ceramic composition, and in particular to a non-reducing dielectric ceramic composition to be used in multilayer ceramic capacitor, in which a base metal such as nickel is used as internal electrode.

## BACKGROUND OF THE INVENTION

With rapid propagation of various types of electronic devices, there is a tendency that these devices are increasingly produced in compact and lightweight design. In particular, this tendency toward compact and lightweight design is more remarkable in the electronic devices of portable type to be used in camera-integrated video tape recorder, portable telephone set, note-book personal computer, palm-top computer, etc.

In such tendency toward compact and lightweight electronic products, the component parts for these devices are also increasingly produced in compact and lightweight design. The means to mount the electronic components are also changing from the technique for inserting and soldering pins, i.e. electronic parts, to be used in through-hole on conventional type printed board to surface mounting technology (SMT), i.e. the technique for mounting and soldering electronic parts on land of electro-conductive pattern on printed board.

The electronic parts used in this SMT are generally called surface mounting devices (SMD). Not only semiconductor components, but also capacitor, resistor, inductor, filter, etc. are included in them. Among them, small components such as capacitor and resistor are called chip components. The most representative of them is multilayer ceramic capacitor.

Fig. 1 shows a partially cutaway perspective view showing structure of a multi layer ceramic capacitor.

The multilayer ceramic capacitor 1 is in form of rectangular parallelepiped, and terminal electrodes 3 and 4 are mounted on a pair of opposed surfaces of multilayer ceramic capacitor body 1, which is in form of rectangular parallelepiped.

In the multilayer ceramic capacitor main unit 2, four internal electrodes 5, 6, 7 and 8 are formed among laminated BaTiO<sub>3</sub> dielectric layers 9, 10 and 11, and dielectric material layers 12 and 13 made of dielectric material are laminated on upper surface of the internal electrode and lower surface of the internal electrode 8.

Every other of the internal electrodes 5, 6, 7 and 8 are connected to terminal electrodes. That is, the internal electrodes 6 and 8 are connected to a terminal electrode 4, and the internal electrodes 5 and 7 are connected to another terminal electrode 3. As a result, a capacitor is formed, which is connected in parallel between the internal electrodes 5 and 6, between the internal electrodes 6 and 7, and between the internal electrodes 7 and 8.

Each of the terminal electrodes 3 and 4 comprises a conductive layer, on which conductive paste containing glass frit is coated or printed and baked, and a plated layer coated on it or a metal cap press-fitted on it.

To manufacture multilayer ceramic capacitor, electrode paste to serve as an internal electrode is printed on a dielectric ceramic composition sheet, a plurality of such sheets are laminated and thermally pressed, the laminated product thus prepared is sintered in the air and a terminal electrode is mounted on it.

In this manufacturing method, the electrode paste to serve as the internal electrode of the capacitor and the dielectric ceramic composition are fired at the same time. For this reason, the material to be used as the internal electrode must have such property that the electrode is formed at the sintering temperature of the dielectric ceramic composition and there occurs no oxidation or no reaction with the dielectric ceramic composition when heated in the air.

As the material to meet the above requirements, noble metal such as platinum, palladium, etc. have been used in the past. However, these noble metals are very expensive and constitute major cause for the high cost of the multilayer ceramic capacitors.

In this connection, attempts have been made to use base metal such as nickel as internal electrode, while nickel is oxidized when it is fired in oxidizing atmosphere and also reacts with the dielectric ceramic composition. This hinders the formation of electrode.

A method to fire nickel in non-oxidative atmosphere to prevent oxidation is disclosed in the specification of U.S. Patent No. 4,241,378, while, in this method, dielectric ceramic composition is reduced and specific resistance is extremely lowered. Thus, it is not suitable for the practical use as capacitor.

As a dielectric ceramic composition having satisfactory dielectric property such as dielectric constant (relative permittivity),  $\text{BaTiO}_3$  dielectric ceramic composition containing  $\text{CaZrO}_2$ ,  $\text{MnO}$ , etc. is disclosed in Japanese Patent Laid-Open Publication 62-2408, whereas this dielectric ceramic composition is fired in non-oxidizing atmosphere when it is reduced and has shorter life time.

5 The multilayer ceramic capacitor is manufactured through the following processes.

- (1) Raw materials are weighed and blended so that composition after firing complies with the predetermined blending ratio.
- (2) Wet mixing and pulverizing are performed.
- (3) Dehydration and drying are performed.
- 10 (4) Adequate quantity of organic binder is added, and it is mixed and turned to enameled.
- (5) This is coated on film by doctor blade method to form dielectric ceramic composition sheet.
- (6) On the dielectric ceramic composition sheet thus prepared, nickel paste to serve as a material for internal electrode is formed by printing.
- (7) The product is laminated and thermally pressed to obtain a multilayer product.
- 15 (8) The product is cut into a predetermined shape.
- (9) Binder removal processing is performed.
- (10) While controlling oxygen partial pressure, the product is fired.
- (11) Re-oxidation is performed in neutral atmosphere.
- (12) Terminal electrode is mounted.

20 As a non-reducing dielectric ceramic composition having longer life time, a dielectric ceramic composition containing  $\{\text{Ba}_A, \text{Ca}_{(1-A)}\}\text{SiO}_3$  (where  $0 \leq A \leq 1$ ) (hereinafter referred as "BCG") as an additive to  $\text{BaTiO}_3$ ,  $\text{MnO}$ , and  $\text{Y}_2\text{O}_3$  is disclosed in Japanese Patent Application 3-18261. However, in the multilayer ceramic capacitor produced using this dielectric ceramic composition, capacitance is varied due to temperature change.

25 In addition to the above, non-reducing dielectric ceramic composition is described in Japanese Patent Laid-Open Publications 61-248304 and 57-71866, U.S. Patent 4,115,493, "Dielectric Materials for Base-Metal Multilayer Ceramic Capacitors" (Proceedings of the Electronics Division Fall Meeting, the American Ceramic Society, October 13-16, 1985) by Y.SAKABE, T.TAKAGI, and K.WAKINO.

### 30 SUMMARY OF THE INVENTION

It is an object of the present invention to provide a non-reducing dielectric ceramic composition suitable for producing a multilayer ceramic capacitor, in which decrease of specific resistance and shortening of service life do not occur due to reduction of the dielectric ceramic composition even when nickel to be used for internal electrode is fired in neutral or reducing atmosphere to prevent oxidation, in which capacitance does not vary extensively due to temperature change.

To attain the above object, the non-reducing dielectric ceramic composition comprises 86.32 to 97.64 mols of  $\text{BaTiO}_3$ , 0.01 to 10.00 mols of  $\text{Y}_2\text{O}_3$ , 0.01 to 10.00 mols of  $\text{MgO}$ , and 0.001 to 0.200 mols of  $\text{V}_2\text{O}_5$ .

### 40 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows structure of a multilayer ceramic capacitor; and

Fig. 2 is a flow chart showing manufacturing process of the non-reducing dielectric ceramic composition.

### 45 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following, description will be given on the features of the present invention in connection with embodiments.

50 A flow chart showing manufacturing process of the non-reducing dielectric ceramic composition of the present invention is given in Fig. 2.

- (1)  $\text{BaTiO}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MnO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$ , etc. are weighed and blended to have the composition after firing as shown in Table 1 and Table 2.

Table 1

No.	Composition (mol%)										Fir'g Temp.  T <sub>2</sub> (°C)
	BaTiO <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	MgO	V <sub>2</sub> O <sub>5</sub>	BCG*		X  MnO	Y  Cr <sub>2</sub> O <sub>3</sub>	Z  Co <sub>2</sub> O <sub>3</sub>	X+Y+Z Total Q'ty	
					A	Q'ty					
1	97.69	0	0.02	0.001	0.58	1.95	0.05	0.29	--	0.34	1400
2	97.54	0.20	0.02	0	0.58	1.95	--	0.29	--	0.29	1380
3	96.88	0.58	0.02	0	0.58	1.94	0.29	0.29	--	0.58	1380
4	97.04	0.58	0	0.005	0.58	1.94	0.15	0.29	--	0.44	1380
5	96.25	0.58	0.96	0.005	0.58	1.92	0.29	--	--	0.29	1340
6	96.89	0.58	0.01	0.30	0.58	1.94	0.29	0.29	--	0.58	1340
7	96.61	0.58	0.01	1.00	0.58	1.93	0.29	0.58	--	0.87	1340
8	96.39	0.58	0.96	0.005	0.58	1.93	0.14	--	--	0.14	1300
9	92.68	0.58	4.63	0.002	0.58	1.85	0.28	--	--	0.28	1300
10	95.86	0.01	1.92	0.005	0.58	1.92	0.29	--	--	0.29	1380
11	87.43	0.53	10.00	0.001	0.58	1.77	0.27	--	--	0.27	1300
12	85.95	0.53	11.50	0	0.58	1.76	0.26	--	--	0.26	1300
13	96.48	0.58	0.96	0.005	0.58	1.93	0.05	--	--	0.05	1340
14	96.67	0.29	0.97	0.005	0.58	1.93	0.14	--	--	0.14	1340
15	97.28	0.58	0	0.001	0.58	1.95	--	0.19	--	0.19	1320
16	97.45	0.58	0.02	0	0.58	1.95	--	--	--	0	1320
17	96.51	0.58	0.97	0.005	0.58	1.93	0.01	--	--	0.01	1320
18	95.47	0.57	1.91	0.002	0.58	1.91	0.14	--	--	0.14	1340
19	92.80	0.56	4.64	0.002	0.58	1.86	0.14	--	--	0.14	1340
20	95.47	0.57	1.91	0.050	0.58	1.91	0.14	--	--	0.14	1340
21	95.42	0.57	1.91	0.001	0.58	1.91	--	0.19	--	0.19	1380
22	97.24	0.58	0.05	0.050	0.58	1.94	--	0.19	--	0.19	1380
23	95.42	0.57	1.91	0.030	0.58	1.91	--	0.19	--	0.19	1360

\*BCG: {Ba<sub>x</sub>Ca<sub>(1-x)</sub>}SiO<sub>3</sub>

Table 2

No.	Composition (mol%)										Fir'g Temp.  T <sub>2</sub> (°C)
	BaTiO <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	MgO	V <sub>2</sub> O <sub>5</sub>	BCG <sup>*</sup>		X  MnO	Y  Cr <sub>2</sub> O <sub>3</sub>	Z  Co <sub>2</sub> O <sub>3</sub>	X+Y+Z Total Q' ty	
					A	Q' ty					
24	95.42	0.57	1.91	0.003	0.58	1.91	--	0.19	--	0.19	1360
25	95.42	0.57	1.91	0.010	0.58	1.91	--	0.19	--	0.19	1360
26	95.48	0.57	1.91	0.240	0.58	1.90	0.14	--	--	0.14	1360
27	96.53	0.39	0.96	0.190	0.58	1.93	--	0.19	--	0.19	1360
28	97.26	0.58	0.01	0.002	0.58	1.95	--	0.20	--	0.20	1320
29	95.05	0.95	0.90	0.002	0.58	1.91	--	0.19	--	0.19	1360
30	91.58	4.58	1.83	0.002	0.58	1.83	--	0.18	--	0.18	1340
31	86.32	10.00	1.75	0.005	0.58	1.75	--	0.18	--	0.18	1340
32	85.39	11.00	1.72	0.001	0.58	1.72	--	0.17	--	0.17	1340
33	98.14	0.59	0.98	0.001	0.58	0	0.29	--	--	0.29	1380
34	97.64	0.59	0.98	0.001	0.58	0.50	0.29	--	--	0.29	1320
35	93.54	0.56	0.94	0.001	0.58	4.68	0.28	--	--	0.28	1340
36	88.30	0.54	0.89	0.001	0.58	10.00	0.27	--	--	0.27	1300
37	85.79	0.53	0.88	0.001	0.58	12.54	0.26	--	--	0.26	1300
38	96.40	0.58	0.10	0.001	0.58	1.93	0.31	0.68	--	1.00	1360
39	92.51	0.74	0.09	0.001	0.58	5.55	0.65	0.46	--	1.11	1360
40	96.11	0.58	0.96	0.001	0.58	1.92	--	0.29	0.14	0.43	1360
41	96.11	0.58	0.96	0.001	0.58	1.92	0.14	--	0.29	0.43	1320
42	97.19	0.58	0.05	0.001	0.58	1.94	0.05	--	0.19	0.24	1360
43	91.85	4.58	1.83	0.002	1.0	1.83	--	0.18	--	--	1390
44	91.58	4.58	1.83	0.002	0.7	1.83	--	0.18	--	--	1360
45	91.58	4.58	1.83	0.002	0.3	1.83	--	0.18	--	--	1340
46	91.58	4.58	1.83	0.002	0	1.83	--	0.18	--	--	1340

\*BCG: {Ba<sub>x</sub>, Ca<sub>(1-x)</sub>}SiO<sub>3</sub>

As the starting materials, BaTiO<sub>3</sub> is used, which is obtained by blending BaO and TiO<sub>2</sub> at molar ratio of 1 : 1 and by chemical reaction at 900 °C to 1200 °C. As this BaTiO<sub>3</sub> powder (50 % of the particles being in particle size 0.8 μ to 1.2 μ) prepared by solution method, or BaTiO<sub>3</sub> obtained from BaCO<sub>3</sub> and TiO<sub>2</sub> pulverized by atomizer to particle size of about 1 μ m may be used.

(2) Wet mixing and pulverizing are performed.

(3) Dehydration and drying are performed.

(4) Adequate quantity of organic binder is added and mixed to turn it to enameled.

(5) The material thus prepared is coated on film in thickness of  $20\text{ }\mu\text{m}$  by doctor blade method, and dielectric ceramic composition sheet is prepared.

(6) Nickel paste used as the material for internal electrode is printed on the dielectric ceramic composition sheet.

(7) This is laminated in five layers and thermally pressed to prepare a multilayer product.

(8) The multilayer product thus prepared is cut into 3216 shape, i.e. in size of  $3.2\text{ mm}$  (length)  $\times$   $1.6\text{ mm}$ .

(9) Stabilizing at  $250^\circ\text{C}$  to  $300^\circ\text{C}$ , binder removal processing is performed for 10 hours.

(10) Oxygen partial pressure is controlled to  $7 \times 10^{-9}$  to  $9 \times 10^{-13}\text{ atm}$ , and stabilizing at firing temperature  $T_2 = 1,200^\circ\text{C}$  to  $1,300^\circ\text{C}$ , it is fired for 2 hours.

(11) Stabilizing at  $700^\circ\text{C}$  to  $1,200^\circ\text{C}$  in neutral atmosphere, re-oxidation is performed for 9 hours.

(12) A terminal electrode of indium-gallium (In-Ga) alloy is mounted on it.

The capacitor thus prepared has capacitance of  $20\text{ pF}$  in each layer, being  $100\text{ pF}$  in total.

On the specimen capacitors prepared as above, electrical properties such as dielectric constant  $\epsilon$ , dielectric loss  $\tan \delta$ , insulation resistance  $IR\text{ }(\Omega)$ , temperature characteristic of capacitance  $T \cdot C\text{ }(\%)$ , and life time  $\mu$  (hour) were determined. The results are shown in Tables 3 and 4.

Table 3

No.	$\epsilon_s$	$\tan \delta$	IR ( $\Omega$ )	T-C(%)				$\mu$ (hour)
				-55°C	-25°C	85°C	125°C	
1	Difficult to sinter							
2	3390	2.6	$5 \times 10^{10}$	-13.2	- 8.0	- 8.5	- 1.0	3
3	3800	2.2	$8 \times 10^{10}$	- 5.0	- 4.0	0	6.0	4
4	3920	2.8	$2 \times 10^{10}$	-16.8	-12.7	- 7.0	- 1.3	9
5	3600	1.9	$5 \times 10^{11}$	-13.2	- 7.8	- 5.4	2.0	100
6	2100	2.3	$5 \times 10^9$	-12.0	- 7.5	- 5.4	- 3.1	7
7	1400	5.4	$8 \times 10^7$	-10.9	- 6.0	- 1.0	2.8	3
8	3100	2.0	$2 \times 10^{11}$	-14.2	- 9.0	- 4.0	- 1.0	90
9	2900	1.8	$3 \times 10^{11}$	- 8.0	- 5.3	- 8.5	- 4.0	34
10	3250	1.8	$3 \times 10^{11}$	- 8.4	- 5.8	- 6.4	- 1.7	31
11	2560	1.6	$1 \times 10^{11}$	- 7.6	- 5.3	- 9.6	- 8.7	37
12	1810	1.4	$1 \times 10^{11}$	- 8.9	- 5.3	-11.4	-13.4	0
13	2820	2.2	$2 \times 10^{11}$	-15.0	- 9.8	- 1.1	2.0	36
14	3180	2.6	$2 \times 10^{11}$	-14.8	- 8.7	3.7	0	29
15	3790	5.9	$2 \times 10^{11}$	-17.8	-11.9	- 1.0	2.0	45
16	Turned to semiconductor state							
17	3000	1.8	$2 \times 10^{10}$	-14.8	- 9.8	0	12.5	39
18	3180	1.8	$3 \times 10^{11}$	- 8.6	- 6.2	- 5.1	1.0	60
19	3050	2.2	$1 \times 10^{11}$	-10.2	- 6.1	- 7.8	- 3.7	48
20	2480	1.5	$2 \times 10^{11}$	-11.7	- 8.4	- 4.4	4.6	200
21	3210	2.0	$2 \times 10^{11}$	- 7.4	- 5.1	- 6.3	0	25
22	2800	2.2	$3 \times 10^{10}$	- 8.3	- 6.1	- 6.4	1.0	150
23	3000	2.2	$1 \times 10^{11}$	- 5.7	- 3.3	- 7.8	- 3.8	110

Table 4

No.	$\epsilon_s$	$\tan \delta$	IR ( $\Omega$ )	T·C(%)				$\mu$ (hour)
				-55°C	-25°C	85°C	125°C	
24	3180	2.1	$2 \times 10^{11}$	- 8.5	- 5.0	- 5.0	4.0	52
25	3260	2.1	$1 \times 10^{11}$	- 7.9	- 5.5	- 6.2	2.0	100
26	2480	1.8	$8 \times 10^9$	-10.6	- 7.9	- 6.1	0	6
27	3100	1.9	$3 \times 10^{10}$	- 8.5	- 6.2	- 7.5	- 3.2	200
28	3010	3.0	$2 \times 10^{11}$	-15.0	- 9.8	- 2.4	- 3.4	33
29	3150	2.0	$3 \times 10^{11}$	- 8.5	- 5.9	- 6.3	- 2.0	28
30	2950	1.9	$2 \times 10^{11}$	-10.5	- 8.7	- 4.4	- 5.0	25
31	2650	1.6	$3 \times 10^{11}$	- 7.5	- 5.4	- 3.8	- 9.0	46
32	Turned to semiconductor state							
33	4330	5.2	$1 \times 10^{11}$	-35.2	-20.0	-11.3	-18.5	8
34	3210	1.7	$3 \times 10^{11}$	-15.0	-10.0	0	7.5	28
35	2880	1.9	$1 \times 10^{11}$	-13.0	- 6.1	- 6.5	- 4.0	40
36	2610	1.6	$2 \times 10^{11}$	- 8.9	- 7.0	- 6.0	- 5.5	38
37	1910	1.4	$3 \times 10^{11}$	- 5.0	- 4.0	- 3.0	- 5.0	9
38	2680	1.2	$2 \times 10^{10}$	- 6.9	- 3.5	- 2.5	- 4.8	85
39	1380	1.0	$4 \times 10^9$	- 4.6	- 2.6	- 8.0	- 9.0	7
40	3080	1.9	$1 \times 10^{11}$	-13.8	-10.0	- 9.0	- 8.5	35
41	2980	2.0	$7 \times 10^{10}$	-11.8	- 7.4	- 4.6	- 1.9	36
42	3850	3.0	$4 \times 10^{10}$	-14.9	- 8.9	- 7.8	- 4.0	40
43	3160	2.2	$2 \times 10^{11}$	-11.5	- 9.0	- 2.0	- 7.0	35
44	3120	2.0	$1 \times 10^{11}$	-10.6	- 8.4	- 4.9	- 5.0	30
45	3000	2.0	$3 \times 10^{11}$	-14.5	-10.0	- 7.0	- 8.5	25
46	2850	1.4	$3 \times 10^{11}$	-14.9	- 9.8	- 5.0	- 9.8	26

Here, dielectric constant  $\epsilon_s$  and dielectric loss  $\tan \delta$  are the values at 20°C and frequency of 1 kHz.  
 The insulation resistance IR is measured at 20°C after voltage of 50 V has been applied for 30 seconds,  
 and temperature characteristic of capacitance T·C is temperature characteristic to capacitance at 20°C of  
 the capacitance at each temperature, and life time  $\mu$  is accelerated life time, applying voltage of 200 V at  
 200°C.



In the evaluation of the above measurements, the values were considered as satisfactory if dielectric constant  $\epsilon$  is 2,500 or more, dielectric loss  $\tan \delta$  is 3.0 or less, insulation resistance IR is  $10^{10}\Omega$  or more, temperature characteristic of capacitance  $T \cdot C$  is within  $\pm 15\%$ , and life time  $\mu$  is 10 hours or more. If the values do not comply with these criteria, the product was considered as defective.

The product which was difficult to sinter or was turned to semiconductor state was considered as defective because such is not suitable for the use as capacitor.

As the result of the evaluation in accordance with the above criteria, the specimens Nos. 5, 8, 9, 10, 11, 13, 14, 17, 18, 19, 21, 22, 23, 24, 25, 27, 28, 29, 30, 31, 34, 35, 36, 38, 40, 41, 42, 43, 44, 45, and 46 were judged as satisfactory, and the specimens Nos. 1, 2, 3, 4, 6, 7, 12, 15, 16, 20, 26, 32, 33, 37, and 39 were judged as defective.

Based on the results of the above judgment, the composition range is defined as follows:

In case  $Y_2O_3$  is less than 0.01 mol% (specimen No. 1), it is difficult to sinter even when the firing temperature ( $T_2$ ) =  $1,400^\circ C$  and is not suitable for practical use. In case it exceeds 10.0 mol% (specimen No. 32), the composition is reduced and is turned to semiconductor state. Thus, it does not act as a dielectric substance.

Therefore, to obtain satisfactory results,  $Y_2O_3$  must be within the range of 0.01 to 10.0 mol%.

In case MgO is contained by less than 0.01 mol% (specimens Nos. 4 and 15), temperature characteristic of capacitance  $T \cdot C$  is aggravated to more than  $\pm 15\%$ , and dielectric loss  $\tan \delta$  may be as high as 5.9. In case it exceeds 10.0 mols (specimen No. 12), accelerated life time is extremely aggravated.

Therefore, to obtain satisfactory results, MgO must be within the range of 0.01 to 10.0 mol%.

When  $V_2O_5$  is added by more than 0.001 mol% (all specimens except Nos. 2, 3, 12 and 16), accelerated life time is extensively improved. In case it is added by more than 0.20 mol% (specimens Nos. 6, 7 and 26), dielectric constant  $\epsilon$  is 2500 or less and insulation resistance is  $1 \times 10^{10}\Omega$  or less, and the product is not suitable for practical use.

Therefore, to obtain satisfactory results,  $V_2O_5$  must be within the range of 0.001 to 0.20 mol%.

In case  $\{Ba_A, Ca_{(1-A)}\}SiO_3$  (where  $0 \leq A \leq 1$ ) is added by less than 0.5 mol% (specimen No. 33) as the additive BCG, temperature characteristic of capacitance is more than  $\pm 15\%$ . In case it exceeds 10 mol % (specimen No. 37),  $\epsilon$  is 2500 or less.

Therefore, to obtain satisfactory results, the additive BCG must be within 0.5 to 10 mol %.

In case total quantity of  $MnO \cdot Cr_2O_3 \cdot Co_2O_3$  is less than 0.01 mol % (specimen No. 16), the composition is turned to semiconductor state. In case it exceeds 1.0 mol % (specimen No. 39), insulation resistance is  $1 \times 10^{10}\Omega$  or less.

Therefore, to obtain satisfactory results, total quantity of  $MnO \cdot Cr_2O_3 \cdot Co_2O_3$  must be within the range of 0.01 to 1.0 mol %.

By the non-reducing dielectric ceramic composition according to the present invention within composition range as described above, it is possible to obtain multilayer ceramic capacitor, in which decrease of specific resistance and shortening of service life due to reduction of dielectric ceramic composition, even when nickel used as internal electrode is fired in neutral or reducing atmosphere to prevent oxidation and capacitance does not vary extensively due to temperature change.

## Claims

1. A non-reducing dielectric ceramic composition, comprising:

86.32 to 97.64 mol  $BaTiO_3$  ;

0.01 to 10.00 mol  $Y_2O_3$

0.01 to 10.00 mol MgO; and

0.001 to 0.200 mol of  $V_2O_5$  .

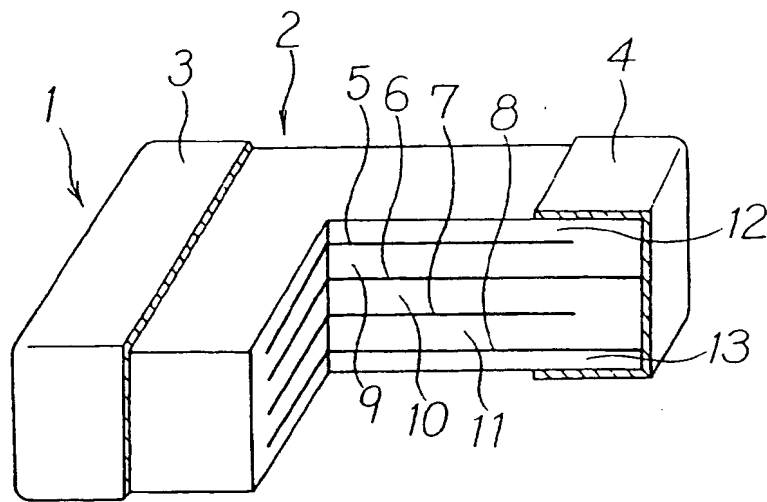
2. A non-reducing dielectric ceramic composition according to claim 1,

wherein 0.01 to 1.0 mol% of at least one or more of  $MnO$ ,  $Cr_2O_3$ , or  $Co_2O_3$  is contained as additive.

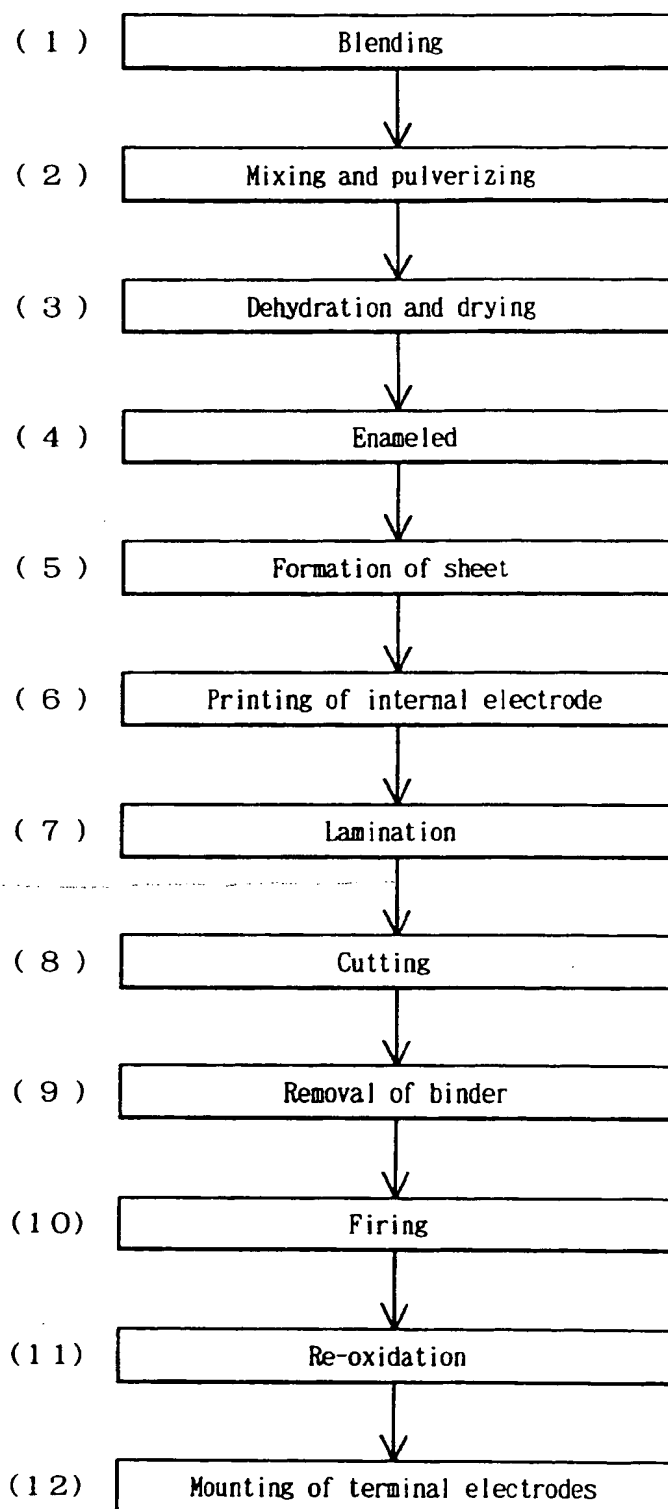
3. A non-reducing dielectric ceramic composition according to Claim 1 or 2,

wherein 0.5 to 10.0 mol% of  $\{Ba_A, Ca_{(1-A)}\}SiO_3$  (where  $0 \leq A \leq 1$ ) is contained as additive.

Fig. 1



F i g . 2



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**D-81679 München (DE)**(54) **Non-reducing dielectric ceramic composition.**

(57) To provide a non-reducing dielectric ceramic composition for multilayer ceramic capacitor, in which decrease of specific resistance and shortening of life time do not occur due to reduction of dielectric ceramic composition even when it is fired in neutral or reducing atmosphere and capacitance does not vary extensively due to temperature change, the non-reducing dielectric ceramic composition according to the present invention comprises 86.32 to 97.64 mols of BaTiO<sub>3</sub>, 0.01 to 10.00 mols of Y<sub>2</sub>O<sub>3</sub>, 0.01 to 10.00 mols of MgO, and 0.001 to 0.200 mol of V<sub>2</sub>O<sub>5</sub>. An additive containing 0.01 to 1.0 mol% of at least one or more of MnO, Cr<sub>2</sub>O<sub>3</sub>, or Co<sub>2</sub>O<sub>3</sub>, and further, an additive containing 0.5 to 10.0 mol% of {Ba<sub>A</sub>,Ca<sub>(1-A)</sub>}SiO<sub>3</sub> (where 0 ≤ A ≤ 1) may be added.

**EP 0 615 262 A3**



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## EUROPEAN SEARCH REPORT

Application Number  
EP 94 10 0192

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	US-A-4 642 732 (MASAAKI IKEDA ET AL.) ----	1	H01G4/12 C04B35/46 C04B35/468
A	DATABASE WPI Section Ch, Week 8733, Derwent Publications Ltd., London, GB; Class L02, AN 87-232573 & JP-A-62 157 603 (KYOCERA CORP) 13 July 1987 * abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			H01G C04B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 1 August 1994	Examiner Goossens, A
CATEGORY OF CITED DOCUMENTS			
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